ELSEVIER

Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Chemistry

Procedia Chemistry 8 (2013) 20 – 27

Youth in Conservation of Cultural Heritage, YOCOCU 2012

Laboratory assessment of the performance of new hydraulic mortars for restoration

Nadia Bianco[a]*, Angela Calia[a], Giampiero Denotarpietro[b], Piero Negro[b]

[a]*Istituto per i Beni Archeologici e Monumentali-Consiglio Nazionale delle Ricerche (IBAM-CNR), Prov.le Lecce-Monteroni, 73100 Lecce, Italy*

[b]*Italcementi S.p.A., Str.St. 7 per Mesagne, 72100 Brindisi, Italy*

Abstract

This study concerns the experimental activity for the set-up of new hydraulic mortars for restoration. Different mix were realized with specific attention to the needs required in the restoration field. Two new formulations were selected and their physical-mechanical properties were determined following the standards tests for mortars characterization. The durability of the new products was evaluated by salt ageing tests as well as their performance with respect to the migration of the saline solution within the stone/mortar system in terms of harmfullness.

Selection and peer-review under responsibility of the IA-CS (Italian Association of Conservation Scientists) and University of Antwerp

Keywords: repair mortars, physical-mechanical properties, salt crystallization test, compatibilty with porous stones.

1. Introduction

The main causes of deterioration of historic buildings, are related to the movement of water and saline solutions through the wall [1]. The salts, dissolved in the water that soaks the walls, migrate to the outer surfaces; here, the water evaporates and the salts crystallize [2]. In this case, only an aesthetic damage is produced by the crystallization of salts, because it involves the formation of efflorescences (of varying colour and consistency)

* Corresponding author. Tel.: +39.329.0273413; fax: +39.0832.422.225.
E-mail address: n.bianco@ibam.cnr.it.

Selection and peer-review under responsibility of the IA-CS (Italian Association of Conservation Scientists) and University of Antwerp
doi:10.1016/j.proche.2013.03.004

visible on the surface [3]. On the other hand, when the salt solution does not reach the outer surface (for example due to sudden increases of the temperature), there is a greater damage, that it is related to the formation of subefflorescence. This latter may lead to powdering phenomena: the crystals grow by feeding themselves with the solution present in the capillary network and so, they exert a pressure of "crystallization" on the walls of the capillaries [4], [5].

Salts may have different sources; they can also be introduced in the artefacts by building materials, such as mortars. Therefore, restoration mortars have to ensure low salt's content with respect to the chemical compatibility with pre-existing materials. In addition, the raw materials in mortar's formulations must be as similar as possible to those employed for the preparation of ancient mortars and also preparation techniques should to be similar to the ancient ones. This would be suitable, in order to obtain a good compatibility of the new materials with the original components of the structure [6]. Therefore, key parameters for the tailoring of repair mortars are chemical-physical and mechanical compatibility with pre-existing materials [7] [8]. The first one mainly concerns the formation of secondary products: during the hardening process, mortars should not contain or produce, substances that could induce damage of the surrounding material (especially soluble salts) or produce alterations of its appearance (spots, scales, etc.); from a physical point of view, they shouldn't create a barrier for water and salt's migration towards the surface of the masonry. With regard to the mechanical compatibility, it mainly refers to the resistance: mortars should not be more resistant than building material and should ensure a "sacrifice function". Finally, durability performance are also needed for mortar's use in repair works. Specifications for plastering and masonry mortars are contained in the EN standards, respectively EN 998-1 [9] and EN 998-2 [10]; therefore, no specific standards currently exist for preparation of mortars responding to the specific needs in the restoration field. The only products whose specifications pay attention to some aspects of interest in restoration works, such as presence of salts, transport of water and porosity features are the Renovation mortars within the UNI-EN 998-1("R" mortar) and WTA recommendation [11]. High porosity, high vapour permeability and reduced capillary action are required to this mortar, suitable for indoor/outdoor plaster on masonry in presence of water and soluble salts.

With respect to the salts problem, the situation is somewhat complex. While threshold values for walls' salt content have been identified by technical bodies in some European countries [12][13][14], on the contrary there's a lack of specific standards providing reference threshold values for the content of soluble salts within the restoration products.

Generally, this lack of specific standards involves the presence on the market of products generically classified as "suitable for restoration of buildings of historic and artistic interest", corresponding to different kinds of mortar on the basis of their properties (CS; M; W) and use (R, GP, G) [9] [10]. Products responding to WTA recommendation [11] and "bio" mortars are also present on the market. The most used binders are hydraulic limes, mainly natural, (NHL 2 - 3.5 and 5) [15] and only in some cases aerial limes are employed; sometimes natural pozzolana is added.

We examined data sheets of these products, in order to find parameters for salts quantification, material's resistance to their crystallization, standard tests or methodologies for their determination. In almost all cases, generic indications was found about the content (free, low, very low salt content, high or total resistance to salts, good resistance to sulphates and chlorides, low tendency to the formation of efflorescences, aggregates and additives free of soluble salts) and/or standard or procedures of tests and analyses.

2. Experimental

The experimental part of this study concerns the set-up of new hydraulic mortars for restoration of soft and porous stone masonry, with the specific function of plastering and ashlars binding .

Two experimental formulations were tested following the standard tests for physical-chemical mortar characterization. Particular attention was paid to the study of their performance in presence of soluble salts.

The durability of the new products was evaluated by salt ageing tests. Morphological changes by photographic recording, weight variations of the specimens and ultrasonic wave velocity propagation were measured during the ageing tests. The assessment of the harmfulness of the mortar application on the stone supports with respect to the transport of the saline solution and salt crystallization effects was also carried out on composite specimens (mortars and underlying stones) [16].

2.1. Set up of new mortars

For the development of the new mortar formulations, different mixes of raw materials were realized. The specifications of the “R” mortar (EN 998-1 Standard), as well as those of the “Renovation mortar systems”(WTA recommendation [11]), that partially meet some specific needs in the restoration field, were assumed as reference parameters for the evaluation of the new products.

We tested recipes with calcic lime (CL), hydraulic lime (HL), or natural hydraulic lime (NHL) as binders [15]. Calcareous sand was chosen for the aggregate fraction for several reasons (large availability of this material in the local area, traditional use in ancient mortars, affinity with the stone supports). Four different granulometric fractions were selected: impalpable, 1.2 mm, 1.6 mm and 2.5 mm (as the maximum grain size).

Microsilica, or white cement, or metakaolin were added as fillers (2% of the mix). Microsilica (SiO_2) is a non-crystalline very fine grey silica powder. Metakaolin is characterized by a significant pozzolanic activity and it is obtained from calcination at 600° C of the kaolin (1):

$$\underset{\textit{Kaolin}}{Al_2O_32SiO_22H_2O} \rightarrow \underset{\textit{metakaolin}}{Al_2O_32SiO_2} + 2H_2O \tag{1}$$

The white cement was *Italbianco 52.5 R*, by Italcementi; the metakaolin was *Metastar 402* by IMERYS Minerals [17]; the microsilica was *Elkem Microsilica Grade 940* by Elkem [18].

Additives with various functions were used (air-entraining, thickeners, fluidifying, surfactant, agents for waterproofing or water retention), never exceeding 1% of the total components.

With regard to the binders, different formulations based on natural hydraulic lime (NHL), on hydraulic lime (HL) and calcic lime (CL) were tested. Each formulation was realized following the EN 1015-2 Standard [19], by different mix ratios of the components (binder, aggregate, additives, water). The calcic lime (CL) and the hydraulic lime (HL) based mortars were excluded because of their poor workability.

Therefore, the following NHL based mixes underwent to the determination of the properties on fresh and hardened samples:

- NHL + calcareous sand + additives
- NHL + calcareous sand + additives + white cement
- NHL + calcareous sand + additives + metakaolin
- NHL + calcareous sand + additives + microsilica

2.2. Characterization of the new formulations

All the NHL based formulations underwent to the evaluation of consistency [20], bulk density [21] and air content [22] on fresh samples, giving acceptable values with reference to the WTA recommendation [11]. Furtherly the preparation of the specimens (16x4x4 cm), as by the UNI Standard [23], was carried out for the determination of the properties on the hardened samples.

The mortar samples were subjected to compressive and flexural strength [23], dry bulk density [24] and water vapour permeability [25]. The screening of the experimental products was made with reference to the parameters set by the 998-1 UNI Standard for “R” mortar (Tab.1). Only two formulations (MO4 and MO5, with the addition of white cement and metakaolin, respectively) met the requirements of the “R” mortars.

On both these formulations the characterization was completed by optical microscopy and ESEM observations [26], Ion Chromatography analyses [27], water absorption by capillarity test; this latter was carried out according the 1015-18 UNI EN Standard [28], that describes a specific procedure for restoration mortars.

Table 1. Results obtained for matured mortars

SAMPLE	MORTAR KIND	FLEXURAL STR.[1] (Mpa) [EN 1015-11]	COMPRESSIVE STR.[2] (Mpa) [EN 1015-11]	DRY BULK DENSITY[3] (Kg/m^2) [EN 1015-10]	WATER VAPOUR PERMEABILITY[4] (µ) [EN 1015-19]
MO4	NHL+aggr.+cem.	0.72	1.51	1.16	9
MO5	NHL+aggr.+met.	0.75	1.91	1.22	10
«R» mortars [13]	--	--	1.5 - 5.0	Declared value	≤ 15

Thin sections and ESEM observations showed (Fig. 1) quite high porosity within both the mortar samples (30-40%); pores are present in the form of air bubbles, clearly showing the effectiveness of the use of the air-entraining additive.

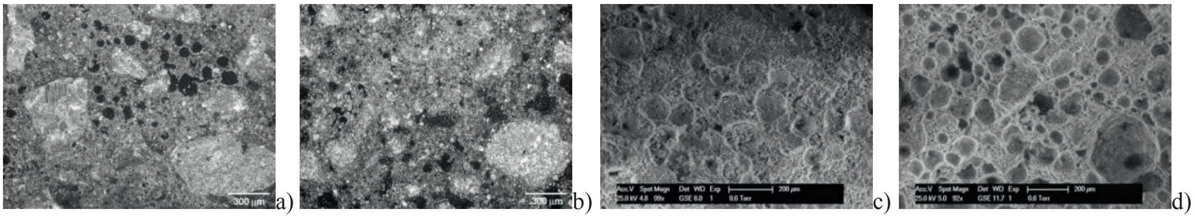


Figure 1. Thin sections of MO4 (a) and MO5 (b). ESEM images of MO4 (c) and MO5 (d).

With regard to Ion Cromatography analyses, the mortar containing metakaolin (MO5) showed a minor salts content (3.71 %) than the mortar with cement (5.01 %).

The water absorption test allowed to qualify as "R" mortar the formulation MO5, while mortar containing cement (MO4) led to a capillary rise over 5mm, appearing completely wet after the test (Fig. 2).

Figure 2. MO4 Samples (on the left) and MO5samples (on the right) after the test of water absorption by capillarity: MO4 samples appear completely wet .

Finally, the adhesion properties of the mortars with respect to the stone substrates were tested [29]. Two soft and porous stones used as traditional building materials in Southern Italy (Apulia region) were chosen, showing different surface roughness, porosity and pore size: *Carovigno Stone* (CS) and *Carparo Stone* (CP). The first is a fine grained white calcarenite, with microscopic pores and porosity about 30%; the second is a coarse yellowish calcarenite, with macropores and porosity about 43%.

The mortar with metakaolin (MO5) showed greater adhesive power on the CP stone (f_u=0.43 N/mm^2) than on the CS stone (0.21 N/mm^2); this latter was recorded for the MO4 mortar on both the stones.

2.3. Durability evaluation by salt decay test

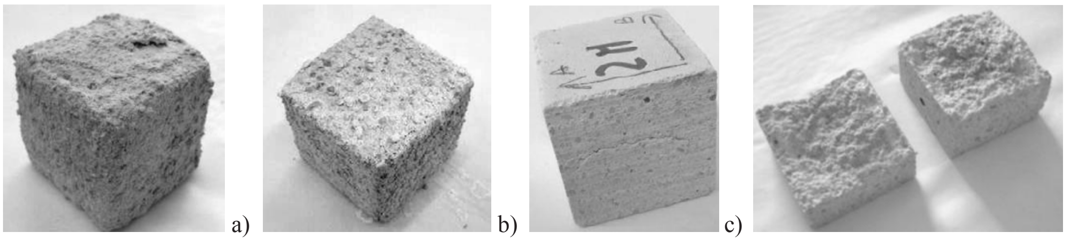
The artificial ageing test was carried out on mortar samples; 5 specimens measuring 4x4x4 cm were prepared for each formulation.

Samples underwent cycles of dissolution and crystallization of salt, using a solution of sodium sulphate (14%), as by the EN 12370 Standard [30]

Salt damage was evaluated by recording the morphology and weight loss of the samples and by the measurement of the ultrasonic wave velocities along x, y and z axes of the specimen.

In mortar samples a homogeneous loss of material took place from the cube faces, the more accentuated for the samples of mortar containing cement (Fig. 3.a and 3.b).

All MO4 samples survived the test (15 cycles); three samples of mortar with metakaolin (MO5) broke between 6 and 8 cycles and the rupture occurred during the phase of immersion in saline solution, starting from a fracture developed parallel to the x-y plane (Fig. 3.c and 3.d):



a) b) c) d)

Figure 3. Samples of MO4 (a) and MO5 (b) after 15 ageing test cycles. Sample of MO5, with the formation of a crack (c) and after breaking (b).

The weight loss was evaluated at the end of every cycle as:

$$\Delta M=((M_f - M_d)/M_d)\cdot 100 \quad (2)$$

where M_f is the mass of the dry sample after each cycle (g), M_d the mass of dry sample before the ageing (g). The result is that the mortar with metakaolin, suffers a minor reduction in weight (about 3%), compared to the one with cement, where weight decreases from 1 to 7%.

In both mortars, the ultrasonic wave velocity increases as the weight of the samples decreases, suggesting cementing action of the salts on sample structure and only surface damage consisting in material loss.

2.4. Evaluation of the saline solution migration within the mortar/stone system

An evaluation of the harmfulness of the mortar layers with respect to the migration of the saline solution within the mortar/stone system was carried out. Composite specimens (n. 12) measuring 14x10x5 cm were made by applying a mortar layer of 1 cm thick on samples (height of 4 cm) of CS and CP stones; then each sample was placed in its container, with the mortar side facing upward and the underlying stone few cm immersed in a sodium sulphate solution (15% of conc.). The surface of the saline solution was sealed with paraffin oil, in order to prevent solution evaporation and to promote its capillary rise through the stone specimens [16]. In this way saline solution is soaked trough the samples by capillary rise and water evaporation through their surface lead to salt crystallization. The effects of the solution evaporation and salt crystallization trough the samples were observed and photographically recorded until the evaporation rate of the solution reached a constant value, that was after 14 days. This was evaluated by weighing the specimen-solution-container system at regular intervals.

During the test it was observed that for mortars + CP specimens the surface of both MO4 and MO5 mortar layers was completely wet between the 1st and the 2nd day. The mortar + CS specimens were instead completely wet between the 3rd and the 4th day. This indicates that the stone structure has the main effect on the control on the water movement trough the samples. The internal structure of the CP better promotes the migration of the solution with respect to the CS stone. Efflorescences appeared after 24 hours (Fig. 5.a) and they increased until 6th day, then remained fairly constant (Fig. 5.b). Any sample showed detachment of the mortar layer from the underlying stone, thus meaning that both mortars do not lead to a barrier effect with respect to the migration of the saline solution towards the sample surface. Nevertheless, a different behavior was showed by the two mortars. The presence of exfoliations was observed on the mortar containing cement (Fig. 4.c), while only efflorescences covered the mortar with metakaolin, with no evidence of disintegration phenomena.

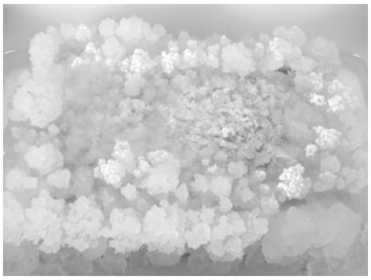
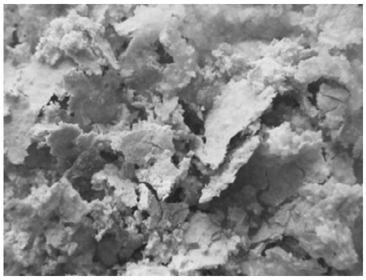

a)

b)

c)

Figure 4. Composite sample (CP + MO4) after 24 hours (a) and at the end of the test (17th day) (b). Detail of the scales on the surface of the mortar with cement (11th day) (c).

3. Conclusion

In this work the set up of new mortars and the assessment of their properties and performance were carried out, paying particular attention to their behaviour in presence of the soluble salts.

A satisfactory evaluation of the suitability of the mortars for restoration use in the cultural heritage field is quite difficult due to the lack of proper reference standard and specifications responding to the necessary requirements in terms of compatibility, harmfulness and effectiveness with reference to the preservation of the pre-existing materials and specific critical conditions, such as the presence of soluble salts. The laboratory assessment was carried out following the standards tests for mortar’s characterization. The specifications of the “Renovation mortar” [9][11], that partially meet some specific needs in the restoration field, were assumed as reference values for the evaluation of the measured parameters.

Similar response was obtained by the two mortars with respect to the compressive and flexural strength, dry bulk density and water vapour permeability. Nevertheless, the mortar with metakaolin (MO5) better meets the specifications of the “R” mortar required by the EN 998-1 Standard than the mortar containing white cement (MO4). Moreover, with respect to the salts action, the MO5 seems less susceptible to the disintegrating effects induced by salt crystallization.

With regard to the harmfulness aspects, both mortars don’t lead barrier effects against the saline solution movement, maintaining their adhesion to the support.

When applied on the same kind of stone they lead the same evaporation rate, thus meaning that the transport of the solution is more controlled by the stone support than by the characteristics of the two different mortars.

The presence of exfoliations was observed on the mortar containing cement, while only efflorescences were present on the surface of the mortar with metakaolin, with no evidence of disintegration phenomena.

Deeper investigation for the qualification of the concerned products for restoration use in the cultural heritage will be carried out by in situ applications

Acknowledgements

The authors would like to thank the staff of Italcementi (Brindisi laboratory), particularly F. Pallara, for the contribution given to the laboratory activity by his experience and willingness.

References

[1] Torraca G. L'attuale stato delle conoscenze sulle alterazioni delle pietre: cause e metodi di trattamento. In: Gnudi C, editor. *La conservazione delle sculture all'aperto: degradazione dei materiali e problemi conservativi*, Ferrara-Bologna (Italy): Alfa; 1969, p. 9-30.
[2] Gasparoli P. *Le superfici esterne degli edifici: degradi, criteri di progetto, tecniche di manutenzione*. 1st ed. Firenze (Italy): Alinea; 2002.
[3] Arnold A, Zehndler K. Salt weathering on monuments. In: Zezza F, editor. *First International Symposium on the Conservation of Monuments in the Mediterranean Basin*, Brescia (Italy): Grafo; 1990, p. 31–58.
[4] Lewin S. The susceptibility of calcareous stones to salt decay. In Zezza F, editor. *La conservazione dei monumenti nel bacino del Mediterraneo. Influenza dell'ambiente costiero e dello spray marino sulla pietra calcarea e sul marmo*, Bari (Italy): Grafo; 1989, p. 59–63.
[5] Rossi Manaresi R, Tucci A. Pore structure and the disruptive or cementing effect of salt crystallization in various types of stone. *Stud Conser* 1991;**36**:53–58.
[6] Moropoulou A, Bakolas A, Moundoulas P, Aggelakopoulou E. Reverse engineering: a proper methodology for compatible restoration mortars. In: Groot C, editor. *Repair mortars for historic masonry*: RILEM; 2009, p. 278-291.
[7] Torraca G. Tecnologia delle malte per intonaci e della conservazione degli intonaci antichi. In Di Francesco C, editor. *Malta, intonaco e colore per la conservazione dei paramenti esterni*, Ferrara (Italy); 1986. p. 65-79.
[8] Lanas J, Alvarez I. Masonry repair lime-based mortars: factors affecting the mechanical behavior. *Cem Concr Res* 2003;**33**:1867–1876.
[9] UNI EN 998-1:2010, Specification for mortar for masonry - Part 1: Rendering and plastering mortar.
[10] UNI EN 998-2:2010, Specification for mortar for masonry - Part 2: Masonry mortar.
[11] WTA Merkblatt 2-9-04/D, Sanierputzsysteme. Wissenschaftlich-Technischen Arbeitsgemeinschaft für Bauwerkserhaltung und Denkmalpflege, 2004.
[12] WTA Merkblatt 4-5-99/D, Beurteilung von Mauerwerk Mauerwerksdiagnostik. Wissenschaftlich-Technischen Arbeitsgemeinschaft für Bauwerkserhaltung und Denkmalpflege, 1999.
[13] ÖNORM B 3355 – 1, Trockenlegung von Feuchtem Mauerwerk - Teil 1: Bauwerksdiagnose und Planungsgrundlagen. Österreichisches Normungsinstitut, 2011.
[14] Fascicules Tecniques. Direction de l'Architecture et du Patrimoine Sousdirection des monuments historiques. Mission études et travaux, 2006.
[15] UNI EN 459-1:2010, Building lime - Part 1: Definitions, specifications and conformity criteria.
[16] Cultrone G, Sebastián E. Laboratory simulation showing the influence of salt efflorescence on the weathering of composite building materials. *Environ Geol* 2008;**56**:729–740.
[17] Imerys Minerals, "Metastar 402," 2011. [Online]. http://www.gianniberti.it/editoriali/vi/MetaStar_402.pdf.
[18] Elkem, "Elkem Microsilica 940," 2011. [Online]. http://www.elkem.com/Global/ESM/quality-safety/product-data-sheets/microsilica/Microsilica-Grade-940-pds-concrete.pdf.
[19] UNI EN 1015-2:2007, Methods of test for mortar for masonry - Part 2: Bulk sampling of mortars and preparation of test mortars.
[20] UNI EN 1015-3:2007, Methods of test for mortar for masonry - Part 3: Determination of consistence of fresh mortar (by flow table).
[21] UNI EN 1015-6:2007, Methods of test for mortar for masonry - Part 6: Determination of bulk density of fresh mortar.
[22] UNI EN 1015-7:2000, Methods of test for mortar for masonry - Part 7: Determination of air content of fresh mortar.
[23] UNI EN 1015-11:2007, Methods of test for mortar for masonry - Part 11: Determination of flexural and compressive strength of hardened mortar.
[24] UNI EN 1015-10:2007, Methods of test for mortar for masonry - Part 10: Determination of dry bulk density of hardened mortar. .
[25] UNI EN 1015-19:2000, Methods of test for mortar for masonry - Part 19: Determination of water vapour permeability of hardened rendering and plastering mortars.
[26] NorMaL 14/83, Sezioni Sottili e Lucide di Materiali Lapidei: Tecnica di Allestimento, Comas Graf. Rome: Commissione Beni Culturali UNI NorMaL, 1983.
[27] UNI 11087:2003, Cultural heritage - Natural and artificial stones - Water soluble salts determination. .

[28] UNI EN 1015-18:2004, Methods of test for mortar for masonry - Determination of water absorption coefficient due to capillary action of hardened mortar.
[29] UNI EN 1015-12:2002, Methods of test for mortar for masonry - Determination of adhesive strength to hardened rendering and plastering mortars on substrates.
[30] UNI EN 12370:2001, Natural stone test methods - Determination of resistance to salt crystallisation.